

SURFACE CHARACTERIZATION OF HYDROGENATED CVD
DIAMOND

UNDERGRADUATE THESIS

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ABSTRACT

Because of its incomparable physical characteristics, diamond has traditionally been a desirable material for industrial applications. Not only is diamond the hardest known naturally occurring mineral, it has an extreme thermal conductivity and a high index of refraction. Recent cost effective methods to synthesize pure, single crystal diamond of significant size have made solid state electronic and optical technologies that utilize diamond more realizable.

Although diamond is intrinsically a bulk insulator, ultra-high vacuum (UHV) hydrogen surface treatment and subsequent exposure to air make diamond a p-type semiconductor. After sputtering hydrogen atoms on the sample surface while heating the diamond, we measured no conductance in vacuum. Upon exposing the sample to air, we found the surface conductance increased by approximately 7 orders of magnitude. Current theoretical models suggest that when water vapor adsorbates from the atmosphere chemically react with the hydrogen, a system of charged surface acceptors forms. Since hydrogenation raises the surface conductivity above the tunneling barrier, atomic scale scanning tunneling microscopy (STM) is being performed to probe the surface topography. The purpose of this study is to examine the formation of the hydrogenated surface layer by atomic force microscopy (AFM) and Raman spectroscopy.

We have also investigated methods to alter the surface resistance with conductive AFM. Once the conducting hydrogen passivated surface layer has been created, electrically insulating oxidized regions can be patterned by applying a bias voltage to the AFM probe. Applications of this scanning probe modification technique include the lithography of a nanoscale field effect transistor (FET) or a single-hole tunneling device. In this respect, diamond's excellent thermal conductivity and wide band gap give it the advantage over other semiconductor materials. These properties are particularly attractive to the radio frequency (RF) industry in which minimal signal distortion in high power and high frequency systems is vital.

1. Introduction

Although diamond is well known as an insulator because of its high covalent bond energy, there are methods to pattern the surface bonds to change its electrical conductivity. In particular, atomic force microscopy (AFM) can be used to control the adsorbate water vapor that collects on the surface of CVD-grown diamond when it is exposed to air. That is, completely terminating the dangling carbon bonds with hydrogen in UHV and then exposing the surface to air results in strong p-type semiconductivity [1]. The thickness of this surface conductive layer has been estimated to be less than 10 nm due to surface band bending that creates a surface hole density of approximately 10^{13} cm^{-2} [2]. It has been shown that the surface conductance of plasma hydrogenated diamond is between $10^{-5} - 10^{-6} \text{ A/V}$ after three days of atmospheric exposure [3]. Others have shown similar results with molecular hydrogen [4]. Since hydrogenation raises the surface conductivity above the tunneling barrier, we intend to characterize the surface for UHV or room temperature atomic scale scanning tunneling microscopy (STM). There have been few STM studies of diamond surface hydrogenation [5], and further examination could clarify the role of hydrogenation in raising the surface conductivity.

On the other hand, an insulating diamond surface is obtained by terminating the dangling bonds with oxygen. Even though the surface of diamond is an insulator already, the separation of these C-H and C-O bonds can be easily controlled. This means the

electrically conductive regions on the surface of diamond can be isolated using oxygen-termination, which is controlled to one monolayer. Moreover, since charge carriers are confined to a 10 nm monolayer, separate conducting regions can be easily isolated without having to add an underlying insulator [6]. Because both of these surface regions are stable in air for several months, more reliable nanoscale transistors can be patterned using conductive AFM [6].

1.1 Control of Atmospheric Adsorbates on Diamond by AFM

Atomic force microscopy is capable of producing high resolution images of height, optical absorption or, in this case, conductivity. By applying a bias voltage to a conductive AFM probe, insulating regions can be patterned on the sample surface of hydrogenated diamond [7]. Applying a 3V bias to the sample surface can localize an insulating area of approximately 60 nm in width and 1-2 nm in height [7]. Nevertheless, when this technique is repeated in a vacuum at approximately 10^{-5} Torr, the bias voltage fails to produce an insulating area. This suggests that the presence of air is required so that the water molecules can adsorb to the surface.

This AFM oxidation method allows for the separation of hydrophobic (oxygen-terminated) regions and hydrophilic (hydrogen-terminated) region. Thus, the adsorption of molecules is precisely controlled. Other such applications of this scanning probe modification technique include the nanofabrication of a field effect transistor or a single-hole tunneling device [8].

1.2 Field Effect Transistors on the Surface of Diamond

Because of the precise control of the scanning probe to pattern the insulating and conducting areas on the surface of diamond, the AFM technique has led to the realization of single-hole and high frequency metal-insulator-metal (MIM) devices. For instance, it has been shown that a single-hole transistor composed of one in-plane-gate FET and two tunneling junctions can be fabricated on the surface of CVD-grown diamond [6]. First, the conducting channel is created by H-termination and then the in-plane gate is obtained by O-termination using an AFM probe. An island, located between the source and the drain, is then isolated by separating the conducting channel by O-termination with two tunneling junctions. The line-width between these two tunneling junctions is less than 30nm [6].

As in any type of FET, current flows from the source to the drain because of the conducting channel. An electric field then controls the conductivity when a voltage is applied between the gate and the source. The primary application of semiconductor FETs is in digital circuitry, in which measurements of peak and valley drain currents are used to switch electronic signals. By applying a drain bias of about 1.4V, desired oscillation peaks with high peak-to-valley current ratios can be observed on the surface of diamond single-hole transistors [6]. Because the single-hole transistor limits itself to the movement of single particles, the precision of the device increases considerably.

Another area where diamond has an advantage over other semiconductor materials is in the RF transistor industry. Diamond's wide bandgap (5.5 eV) gives it a high breakdown field (> 10 MV/cm) [9]. Diamond's extreme thermal conductivity (22 W/cmK) also limits signal distortion in high-power, high-temperature wireless systems. Hydrogenated diamond metal-insulator-semiconductor field-effect-transistors (MISFETS) have been shown to achieve current gain and power gain cutoff frequencies of 45 GHz and 120 GHz and output power densities of 2.1 W/mm [10, 11]. Furthermore, the control of the AFM process to create hydrophobic and hydrophilic regions on the diamond surface could mark the integration of nanotechnology with biotechnology by the fabrication of ion-sensitive field-effect-transistors (ISFETS) [12-14].

2. Experimental Methods

The purpose of these experiments is twofold. The first is to systematically characterize the surface of hydrogenated diamond and to elucidate the role of air in decreasing the surface resistance. The second is to perform a conductive AFM oxidation reaction on the hydrogenated surface and to assess the feasibility of patterning semiconductor-insulator devices on the sample surface. We have studied two CVD 3a diamond samples (0.18in.x0.18in.x0.021in.) from Professor David Awschalom's group at UC-Santa Barbara.

2.1 Ultra-High Vacuum Surface Studies of the Hydrogenated Diamond

We propose a method to hydrogenate and heat the surface of diamond samples in vacuum while measuring the surface resistance. The goal of these measurements is to determine if exposure to air is necessary requisite to forming the semiconducting diamond surface. Figure 1 below includes a schematic of the diamond heater setup. The external pyrometer (Luxtron Photrix) with which we measure the sample temperature in vacuum is not shown in the schematic. In addition, a wobble stick (MDC 60 degree wide angle, 2 inch linear travel) is used to reposition the leads on the sample in situ. That way the surface resistance of the hydrogenated regions can be measured without breaking vacuum.

There are two methods by which we have exposed the sample surface to hydrogen. The first is by using a leak valve to expose the surface to H_2 for 1 hour, while directly heating the sample to 800K with 1.6A from an external power supply. This current and temperature reading were calibrated with the pyrometer. The tantalum wire (Alfa Aesar, 0.25mm diameter) is wound tightly between the bisque alumina sandwich so that the largest resistance drop occurs directly underneath the sample. We use an Extorr mass spectrometer to determine the partial pressure of the gases in UHV. Before exposure the base pressure of the chamber is 7.5×10^{-9} torr, and afterward the partial pressure of the molecular hydrogen peak is 2.5×10^{-5} torr as compared to an air peak of 5×10^{-8} torr. Next, we anneal the surface under hydrogen flux for 2 hours under at 500K

and allow the sample to remain in vacuum for another hour after closing the hydrogen leak valve. Finally, we degas the chamber to air overnight and measure the surface conductance in vacuum after 12 hours. The surface conductance results of this molecular hydrogen study are shown in Figure 3.

The second method we use to create the hydrogenated surface is to expose the surface to atomic hydrogen. We leak in hydrogen gas at the same partial pressures as before and heat the diamond at 800K, but this time we sputter hydrogen atoms onto the sample surface for 20 minutes with a 1kV beam voltage and an emission current of 20mA. We ground the surface clamps to the vacuum chamber so the charge from the sputter current does not accumulate on the sample surface. We also use voltmeters on the molybdenum leads to ensure that the electric field is oriented on the center of the sample. After sputtering, we anneal the sample at 500K for an hour under H_2 flux and allow the sample to remain in vacuum for another hour. As before, we degas the chamber to air overnight and perform resistance measurements the next day.

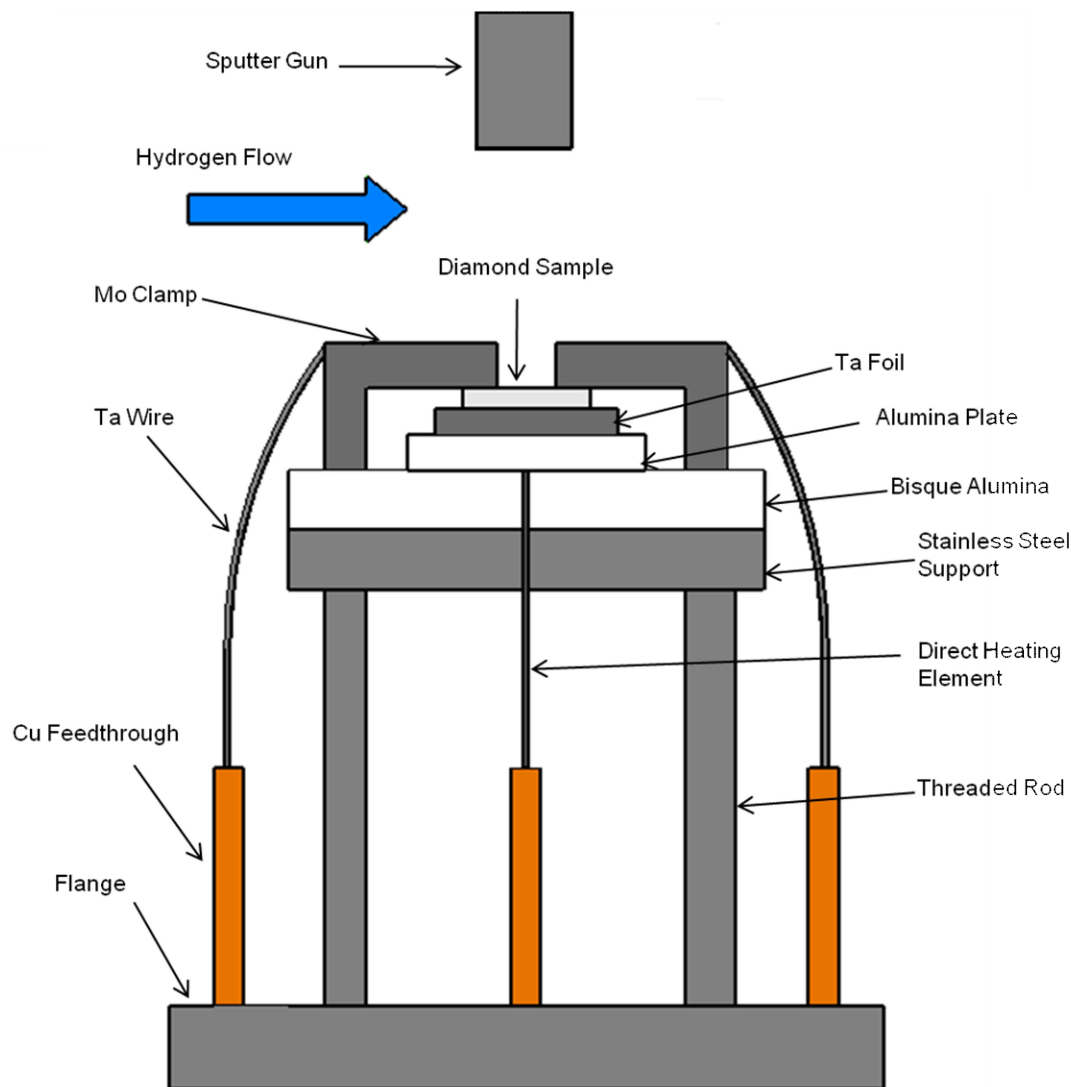


Figure 1: UHV diamond surface hydrogenation setup with home-built UHV diamond heater. Copper feedthroughs (ISI Insulator Seal 30A, 5kV) are used to heat the sample for surface resistance measurements without breaking vacuum. The bisque alumina and alumina plate are used to electrically isolate the sample from the stainless steel supports. Moreover, the alumina is compatible with heating the diamond over 1300 K. The sample is heated by an external power supply hooked up to the feedthroughs. We use molybdenum clamps to hold the diamond in place and to measure the surface resistance in situ. Not shown is the pyrometer, which is used to measure the IR radiation of the tantalum foil beneath the diamond because the CVD samples are transparent. The pyrometer (Luxtron Photrix) converts this IR measurement to a temperature that is approximately equal to the sample temperature because of the high thermal conductivity of diamond. The sputter gun (RBD ion gun, 2kV) is then used to focus the ionized hydrogen atoms directly onto the sample surface.

2.2 Conductive AFM Oxidation Reaction on Hydrogenated Diamond

After the surface of the CVD diamond has been hydrogen passivated, we perform AFM (Ohio State University ENCOMM Veeco Dimension 3000) in non-contact mode to measure the topography of the H-terminated sample. The results of this topography study are shown in Figure 5. We have also performed conductive AFM (NanoInk dip-pen nanolithography at Ohio State University's Nanotech West facility) on this H-passivated, semiconducting diamond surface. Figure 2 below shows a schematic of the conductive AFM oxidation reaction. Applying a bias voltage greater than 3V between the conductive AFM probe and the sample surface breaks the H-terminated dangling carbon bonds on the surface. The oxygen in the air then readily terminates these dangling bonds leaving behind an oxidized, insulating area. While it is beyond the scope of this study, we can selectively localize these insulating surface regions from the rest of the semiconducting H-terminated surface and pattern MIM devices on the surface. This technique requires the use of lithography scripts to precisely control the movement of the voltage biased AFM probe.

Instead of performing this lithographic AFM method, we have investigated the voltage dependence and time characteristics of this AFM oxidation reaction. This experiment is carried out by parking the AFM tip over one H-terminated semiconducting areas on the diamond surface and measuring the current from the contacted tip and the surface at a bias voltage of 1V. We then increase the bias above the threshold ($\sim 3\text{V}$) for

the oxidation reaction to occur and measure the dissipation of the surface current as a function of time. We repeat this measurement for different threshold voltages at various H-terminated areas within 1 micron of each other. The results are shown in Figure 6.

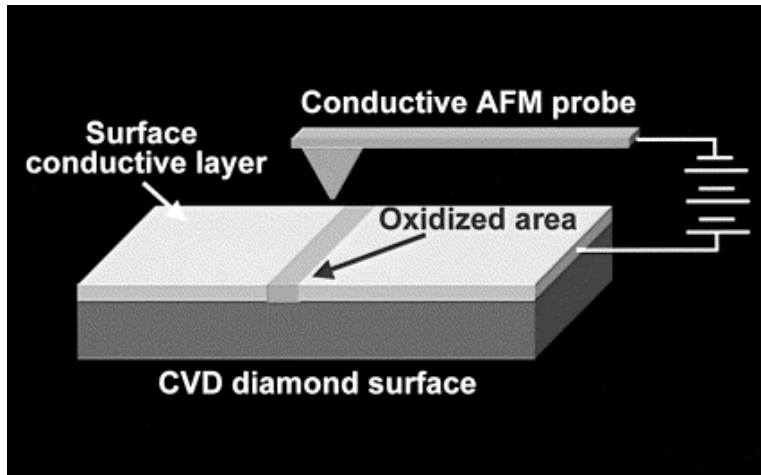


Figure 2: Schematic of conductive AFM setup. When an external applied bias voltage greater than 3V is applied between the conductive AFM probe (contact diamond tip, K-Tek Nanotechnology) and the H-passivated CVD surface, the hydrogen desorbs and the oxygen in the atmosphere terminates the dangling bonds, leaving behind an insulating area. Diagram was adapted from reference [7].

3. Results and Discussion

The first aspect of this study was to investigate the role of air in decreasing the surface conductance of hydrogenated diamond. Figure 3 shows transport measurements taken in UHV after the surface has first been exposed to hydrogen in situ and then subsequently vented to air. The surface conductance results taken in air after this hydrogenation procedure are similar. The results in Figure 3 indicate that the surface resistance is below the tunneling barrier, which means that future STM measurements

could be performed on a clean H-terminated surface. However, because the conductance drops to zero at 77K, low-temperature STM would not be possible on this H-terminated surface.

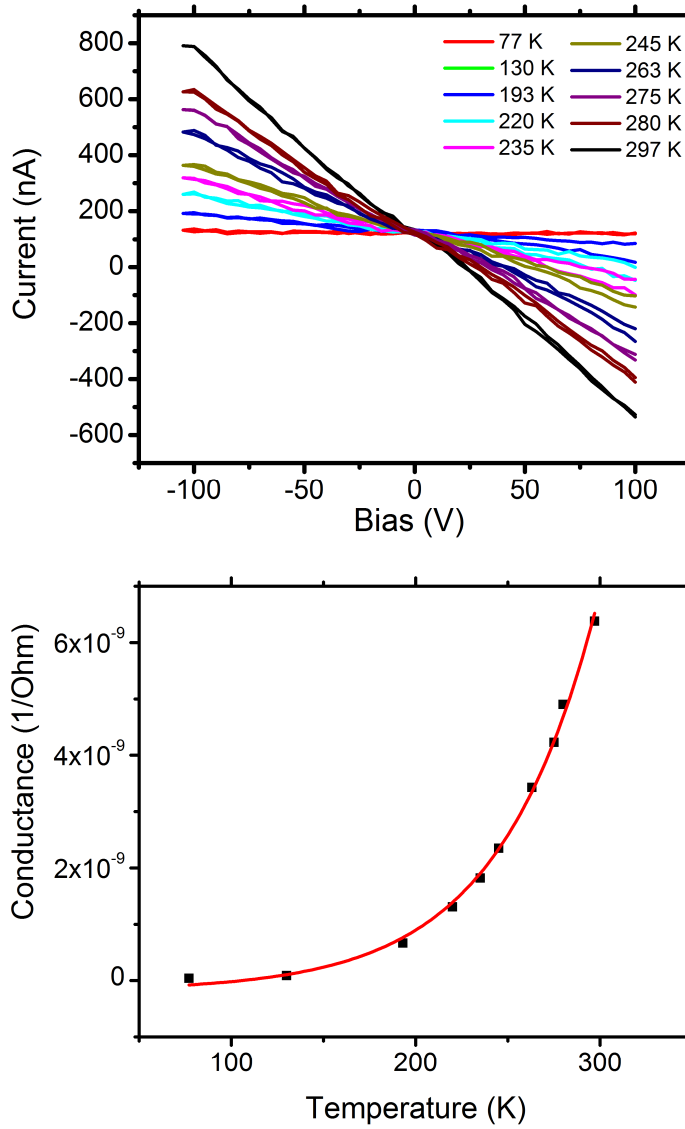


Figure 3: Transport measurements of hydrogenated diamond surface. The sample was exposed to molecular hydrogen for 1 hour while heating in UHV at 800K. After exposing the surface to air, the sample resistivity dropped to $3 \times 10^5 \Omega \cdot m$ in 24 hours. At room temperature, the sample resistance was $22 M\Omega$. IV measurements show that the semiconducting surface is stable in UHV, which is promising for future STM measurements. Even though the sample resistance is above the tunneling barrier, it is highly temperature dependent.

We have also performed Raman spectroscopy on the surface to verify the adsorption of hydrogen by this technique. This process is to ensure that the drop in surface resistance is due to the hydrogenation and not the presence of some other surface specie. Figure 4 shows the spectroscopy results on the untreated, hydrogenated, and hydrogen then oxygen treated sample. The sample was hydrogenated and then oxygen treated because of the easily observable O-H surface stretch bond at 3600 cm^{-1} . While future systematic analysis should be performed to further characterize the spectra, it is clear that the hydrogen is adsorbing on the surface.

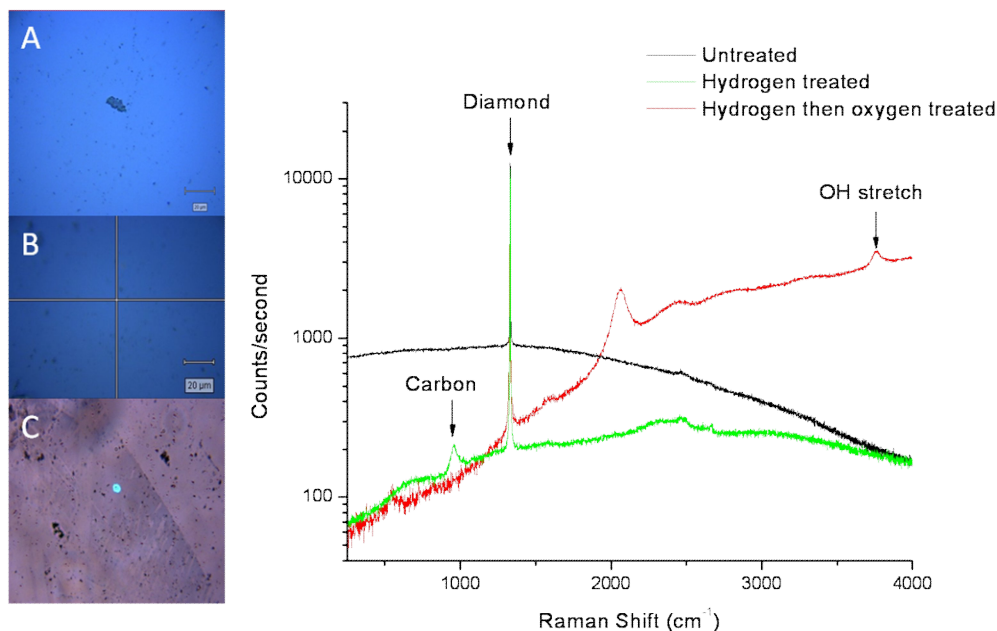


Figure 4: Raman spectroscopy of untreated (A), hydrogen (B), and hydrogen then oxygen treated (C) diamond. Figures to the left indicate the sample locations where spectra were taken. The oxygen treatment was performed in UHV and then examined with the Raman microscope to observe the OH stretch bond. Clearly the spectra indicate the presence of OH surface bonding, and that hydrogen surface treatment and annealing alters the carbon background of the sample. Further systematic analysis is needed to characterize the peak at 2000 cm^{-1} .

In order to elucidate the role of the hydrogen in altering the surface structure of the CVD diamond samples, we performed non-contact AFM before and after hydrogenation. The AFM topography in Figure 5 is for the CVD samples after they have been exposed to air. After hydrogenation, the graphitization marks on the original sample are reduced and the RMS surface roughness decreases by nearly an order of magnitude. This is the case for the atomically sputtered H-terminated diamond and not necessarily the case for the molecular hydrogenated diamond. We believe this is because at temperature below 800K, the etching rate of atomic hydrogen is approximately twice as fast as the graphitization rate, which is caused by the heating of the sample [15].

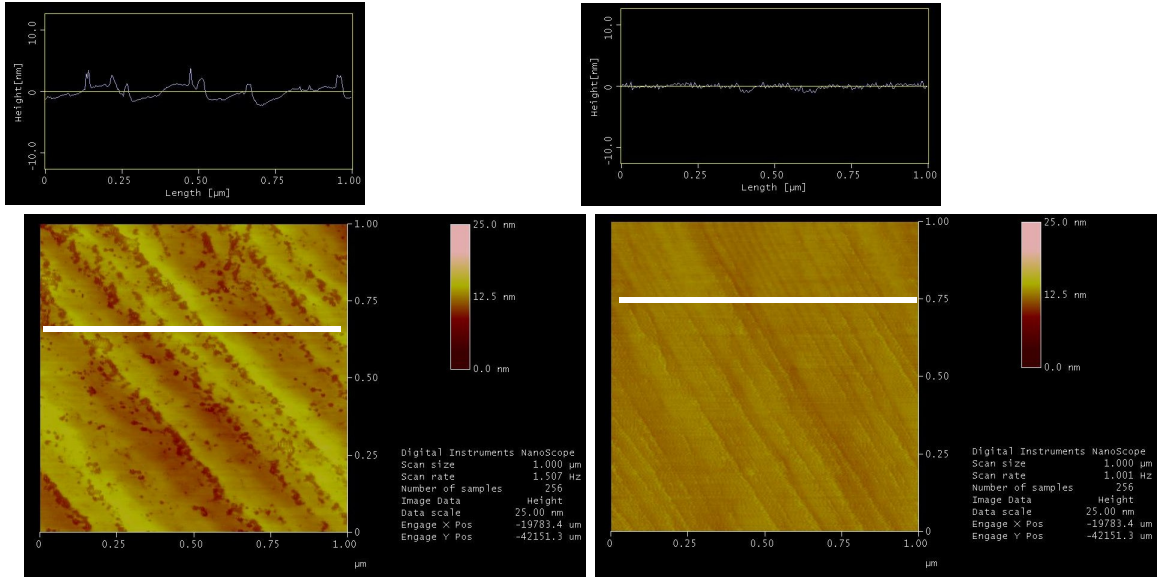


Figure 5: AFM topography before UHV hydrogenation (left) and after UHV hydrogenation (right). The white lines indicate the locations of the cross sectional measurements above. Prior to the H-passivation, the samples are significantly graphitized. Initially, the RMS surface roughness is approximately 5 nm. After sputtering atomic hydrogen on the surface, however, the number of graphite spots is reduced, decreasing the RMS surface roughness to approximately 0.75 nm. This result is promising for future STM measurements of H-passivated CVD diamond.

In order to test the feasibility of patterning the H-passivated CVD diamond surface for device applications, we have investigated the AFM oxidation reaction as a function of time and threshold bias voltage. The results are shown in Figure 6. We plot the current between the tip and the H-passivated semiconducting surface. We measure the current at a 1V bias for four different areas within 1 micron of each other. Because this initial bias voltage is lower than the threshold voltage ($\sim 3\text{V}$) for the oxidation reaction to occur on our hydrogenated surface, we measure the initial current between the contacted tip and the sample to be approximately 65 nA.

By instantaneously stepping up the bias voltage, we have found that the time for complete oxidation to occur is approximately 10 seconds for a 4 V bias and around 2 seconds for 5-7 V biases. This time characteristic of our H-passivated surface agrees with other similar studies that have been performed [16]. In addition to the time characteristic, these voltage dependence curves level off at various points where the oxidation reaction is momentarily halted. It is believed that at a DC bias, there is a positive space charge buildup of hydrogen ions at the oxide-sample interface [16]. This space charge deflects the electric field until the hydrogen ions are completely removed and the reaction reaches steady state again.

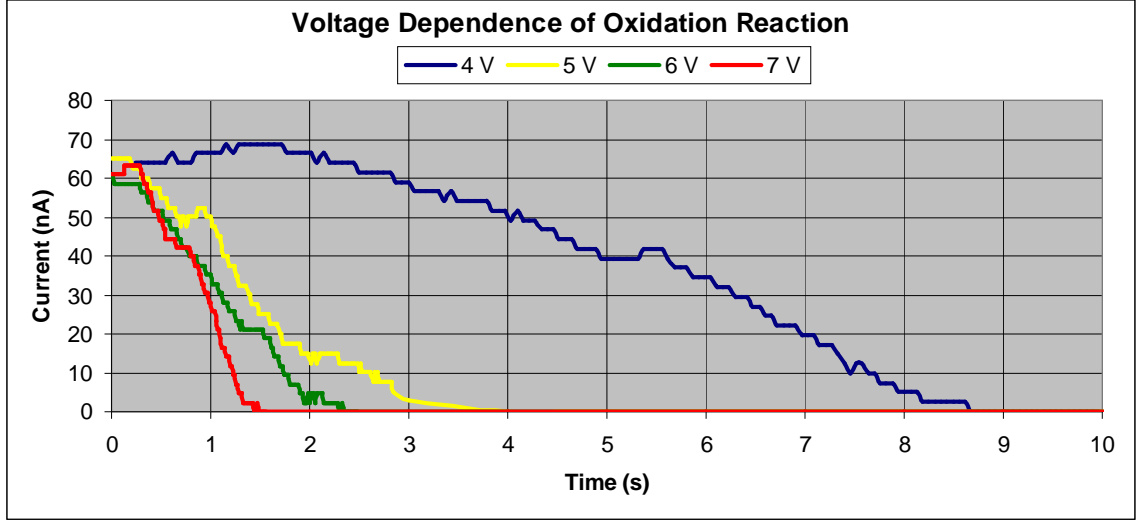


Figure 6: Voltage dependence of the oxidation reaction on the H-passivated CVD diamond surface. The current between the contacted tip and the sample drops as a function of time and bias voltage. The oxidation reaction requires a bias voltage greater than 3V to occur.

4. Challenges and Future Works

The atomic and molecular hydrogenation procedures described in this study have dropped the surface resistance of the CVD diamond samples to approximately $20 \text{ M}\Omega$, which is approximately 2 orders of magnitude higher than the more commonly used hydrogen plasma treatment described elsewhere [3]. Due to lack of availability of a plasma deposition tool, we have characterized the surface of atomic and molecular H-terminated diamond instead. If the atomic and molecular methods do not provide a clean surface for tunneling, this hydrogen plasma technique may provide an alternate means to form the semiconducting diamond surface layer for future STM measurements.

The next step in performing the conductive AFM of the H-passivated sample would be to obtain a conductive AFM image of the current between the tip and the sample at various points over a scan. However, because the current in the H-terminated regions is so small (~ 65 nA), there is not enough auxiliary channel resolution in the AFM to distinguish this from the insulating O-terminated regions. Furthermore, the H-termination on the surface appears to be patchy even with a one micron scan size. For these two reasons, a conductive map of the surface cannot be obtained at this time.

The resolution problem might be resolved by using the voltage output of the external ammeter, instead of the current output, as an auxiliary channel. For example, a pre-amplified 5 V reading on the H-terminated regions would be easily distinguished from the O-terminated background insulating reading. As previously mentioned, the H-terminated plasma treatment might result in a cleaner sample with a more uniform hydrogen passivation, which could solve the second problem. It might also be a matter of exposing the surface to longer hydrogen treatments. If these issues are resolved, it would be possible to potentially pattern electronic devices on the surface of the CVD diamond samples.

5. Conclusions

We have reproducibly formed a p-type semiconducting surface layer on CVD-grown diamond samples and verified that this procedure requires UHV hydrogen treatment and subsequent exposure to air. The surface resistance is below the tunneling

barrier and stable in UHV, which is promising for future STM measurements. However, the surface hole accumulation layer does not conduct at temperatures below 77K meaning low-temperature STM is out of the question. Moreover, we have observed that the atomic hydrogenation procedure forms a nearly atomically smooth surface because graphitization marks are etched away by the hydrogen. In parallel with this surface structure study, we have reproduced the anodic oxidation reaction on the surface of H-passivated CVD diamond using a conductive AFM surface modification technique at bias voltages greater than 3 V. This technique could be promising for future patterning of nanoscale electronic devices on the surface of H-terminated CVD diamond.

References

- [1] M.I. Landstrass and K.V. Ravi. "Hydrogen passivation of electrically active defects in diamond." *Applied Physics Letters* **55**, 975 (1989).
- [2] K. Hayashi, et. al. "Hydrogen depth-profiling in chemical-vapor-deposited diamond films by high-resolution elastic recoil detection." *Applied Physics Letters* **81**, 744 (1997).
- [3] F. Maier, M. Riedel, B. Mantel, J. Ristein, L. Ley. "Origin of surface conductivity in diamond." *Phys. Rev. Lett.* **95**, 3472-3475 (2000).
- [4] F. Fizzotti, et. al. "Diamond surface conductivity after exposure to molecular hydrogen." *Diamond & Related Materials* **16**, 836 (2007).
- [5] L. Hellner, A. J. Mayne, R. Bernard, G. Dujardin. "Hydrogenated diamond crystal C(100) conductivity studied by STM." *Diamond & Related Materials* **14**, 1529-1534 (2005).
- [6] Tachiki, M., et al. "Fabrication of Single-Hole Transistors on Hydrogenated Diamond Surface." *Applied Physics Letters* **81**, 2854 (2002).
- [7] Tachiki, Minoru, et al. "Control of Adsorbates and Conduction on CVD-Grown Diamond." *Applied Surface Science* **159** 578-582 (2000).
- [8] K. Hayashi, S. Yamanaka, H. Okushi, and K. Kajimura, "Surface conductive layers on oxidized (111) diamonds." *Applied Physics Letters* **68** 376 (1996).
- [9] J. E. Field. The Properties of Natural and Synthetic Diamond (Academic Press, London, 1992).
- [10] Kasu, et. al. "Diamond-based RF power transistors: Fundamentals and applications." *Diamond and Related Materials* **16**, 1010 (2007).
- [11] Umezawa, et. al. "RF diamond transistors: Current status and future prospects." *Japanese Journal of Applied Physics* **44**, 7789 (2005).
- [12] Popova, B., W. Kulisch, C. Popov, and C. Hammann. "Immobilization of RNA and Protein Biomolecules on Nanocrystalline Diamond for the Development of New Biosensors." *Functional Properties of Nanostructured Materials* **233** 515-520 (2006).

- [13] Bennett, Andrew, et al. "Diamond Based Ion Sensitive Field Effect Transistors for Cellular Biosensing." *Materials Research Society* **956** 221-227 (2007).
- [14] Nebel, E. Christopher. "DNA-ISFETS from Single Crystalline Diamond." *Materials Research Society* **956** 229-234 (2007).
- [15] C. Cheng, et al. "In situ observation of atomic hydrogen etching on diamond-like carbon films produced by pulsed laser deposition." *Appl. Surf. Sci.* **174** 251-256 (2001).
- [16] K. Sugata, et al. "Nanoscale modification of the hydrogen-terminated diamond surface using atomic force microscope." *Jpn. J. Appl. Phys.* **41** 4983-4986 (2002).